SPECIFICATION

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THERMAL BARRIER COATING MATERIALS

Background of Invention

Field of the Invention

[0001] This invention generally relates to coatings for components exposed to high temperatures, such as the hostile thermal environment of a gas turbine engine. More particularly, this invention is directed to a protective coating for a thermal barrier coating (TBC) on a gas turbine engine component, in which the protective coating has a low thermal conductivity, and may be resistant to infiltration by contaminants present in the operating environment of a gas turbine engine.

Description of the Related Art

[0002] Higher operating temperatures for gas turbine engines are continuously sought in order to increase their efficiency. However, as operating temperatures increase, the high temperature durability of the components within the hot gas path of the engine must correspondingly increase. Significant advances in high temperature capabilities have been achieved through the formulation of nickel and cobalt-base superalloys. Nonetheless, certain components of the turbine, combustor and augmentor sections of a gas turbine engine can be required to operate at temperatures at which the mechanical properties of such alloys are insufficient. For this reason, these components are often protected by a thermal barrier coating (TBC).

[0003]

TBC's are typically formed of ceramic materials deposited by plasma spraying, flame spraying and physical vapor deposition (PVD) techniques. TBC's employed in the highest temperature regions of gas turbine engines are most often deposited by PVD, particularly electron-beam PVD (EBPVD), which yields a strain-tolerant columnar grain

structure that is able to expand and contract without causing damaging stresses that lead to spallation. Similar columnar microstructures can be produced using other atomic and molecular vapor processes, such as sputtering (e.g., high and low pressure, standard or collimated plume), ion plasma deposition, and all forms of melting and evaporation deposition processes (e.g., cathodic arc, laser melting, etc.). In contrast, plasma spraying techniques such as air plasma spraying (APS) deposit TBC material in the form of molten splats, resulting in a TBC characterized by a degree of inhomogeneity and porosity.

[0004] Various ceramic materials have been proposed as TBC's, the most notable of which is zirconia (ZrO_2) that is partially or fully stabilized by yttria (Y_2O_3), magnesia (MgO) or another alkaline-earth metal oxides, or ceria (CeO_2) or another rare-earth metal oxides to yield a tetragonal microstructure that resists phase changes. Still other stabilizers have been proposed for zirconia, including hafnia (HfO_2) (U.S. Patent No. 5,643,474 to Sangeeta) and gadolinia (gadolinium oxide; Gd_2O_3) (U.S. Patent No. 6,177,200 to Maloney). U.S. Patent Nos. 5,512,382 and 5,624,721 to Strangman mention yttria-stabilized hafnia as a possible TBC material, though neither of these patents suggests what a suitable composition or microstructure might be. Still other proposed TBC materials include ceramic materials with the pyrochlore structure $A_2B_2O_7$, where A is lanthanum, gadolinium or yttrium and B is zirconium, hafnium and titanium (U.S. Patent No. 6,117,560 to Maloney). However, yttria-stabilized zirconia (YSZ) has been the most widely used TBC material. Reasons for this preference for YSZ are believed to include its high temperature capability, low thermal conductivity, and relative ease of deposition by plasma spraying, flame spraying and PVD techniques.

[0005] To protect a gas turbine engine component from its hostile thermal environment, the thermal conductivity of a TBC is of considerable importance. Lower thermal conductivities enable the use of a thinner coating, reducing the weight of the component, and/or reduce the amount of cooling airflow required for air-cooled components such as turbine blades. Though the thermal conductivity of YSZ decreases with increasing yttria content, the conventional practice has been to partially stabilize zirconia with six to eight weight percent yttria (6-8%YSZ) to promote spallation resistance. Ternary YSZ systems have been proposed to reduce the thermal

conductivity of YSZ. For example, commonly-assigned U.S. Patent Application Serial No. [Attorney Docket No. 13DV-13490] to Rigney et al. discloses a TBC of YSZ and alloyed to contain certain amounts of one or more alkaline-earth metal oxides (magnesia, calcia (CaO), strontia (SrO) and barium oxide (BaO)), rare-earth metal oxides (ceria, gadolinium oxide, lanthana (La_2O_3), neodymia (Nd_2O_3), and dysprosia (Dy_2O_3)), and/or such metal oxides as nickel oxide (NiO), ferric oxide (Fe_2O_3), cobaltous oxide (CoO), and scandium oxide (Sc_2O_3). According to Rigney et al.; when present in sufficient amounts these oxides are able to significantly reduce the thermal conductivity of YSZ by increasing crystallographic defects and/or lattice strains. Another proposed ternary system based on YSZ and said to reduce thermal conductivity is taught in U.S. Patent No. 6,025,078 to Rickerby et al. The additive oxide is gadolinium oxide, dysprosia, erbia (Er_2O_3), europia (Eu_2O_3), praseodymia (Pr_2O_3), urania (UO_2) or ytterbia (Yb_2O_3), in an amount of at least five weight percent to reduce phonon thermal conductivity.

[0006] Additions of oxides to YSZ coating systems have also been proposed for purposes other than lower thermal conductivity. For example, U.S. Patent No. 4,774,150 to Amano et al. discloses that bismuth oxide (Bi_2O_3), titania (TiO_2), terbia (Tb_4O_7), europia and/or samarium oxide (Sm_2O_3) may be added to certain layers of a YSZ TBC for the purpose of serving as luminous activators.

[0007] To be effective, a TBC must strongly adhere to the component and remain adherent throughout many heating and cooling cycles. The latter requirement is particularly demanding due to the different coefficients of thermal expansion (CTE) between ceramic materials and the substrates they protect, which as noted above are typically superalloys, though ceramic matrix composite (CMC) materials are also used. An oxidation-resistant bond coat is often employed to promote adhesion and extend the service life of a TBC, as well as protect the underlying substrate from damage by oxidation and hot corrosion attack. Bond coats used on superalloy substrates are typically in the form of an overlay coating such as MCrAlX (where M is iron, cobalt and/or nickel, and X is yttrium or another rare earth element), or a diffusion aluminide coating. During the deposition of the ceramic TBC and subsequent exposures to high temperatures, such as during engine operation, these bond coats form a tightly adherent alumina (Al_2O_3) layer or scale that adheres the TBC to the bond coat.

[0008] The service life of a TBC system is typically limited by a spallation event brought on by thermal fatigue. In addition to the CTE mismatch between a ceramic TBC and a metallic substrate, spallation can be promoted as a result of the TBC being contaminated with compounds found within a gas turbine engine during its operation. A notable example is a mixture of several different compounds, typically calcia, magnesia, alumina and silica, referred to herein as CMAS. CMAS has a relatively low melting eutectic (about 1190 ° C) that when molten is able to infiltrate to the cooler subsurface regions of a TBC, where it resolidifies. During thermal cycling, the CTE mismatch between CMAS and the TBC promotes spallation, particularly TBC deposited by PVD and APS due to the ability of the molten CMAS to penetrate their columnar and porous grain structures, respectively.

[0009] It would be desirable if improved TBC materials were available that exhibited low thermal conductivities, and preferably also exhibited resistance to spallation attributable to CMAS infiltration.

Summary of Invention

[0010] The present invention generally provides a coating material, particularly a thermal barrier coating (TBC), for a component intended for use in a hostile thermal environment, such as the superalloy turbine, combustor and augmentor components of a gas turbine engine. The coating material has a cubic microstructure and consists essentially of either zirconia (ZrO_2) stabilized by dysprosia (Dy_2O_3), gadolinium oxide (Gd_2O_3), erbia (Er_2O_3), neodymia (Nd_2O_3), samarium oxide (Sm_2O_3) or ytterbia (Yb_2O_3), or hafnia (HfO_2) stabilized by dysprosia, gadolinium oxide, samarium oxide or ytterbia. Up to five weight percent yttria may be added to the coating materials to further promote thermal cycle fatigue life.

[0011] According to the invention, zirconia and hafnia alloyed with their respective above-noted stabilizers have been shown to have lower thermal conductivities than conventional 6-8%YSZ, allowing for the use of a thinner coating and/or lower cooling airflow for air-cooled components. In addition, the hafnia-based coatings of this invention are resistant to infiltration by CMAS, thereby promoting the life of the TBC by reducing the risk of CMAS-induced spallation. While others have proposed additions of some of the oxides used as stabilizers in the present invention, including

the aforementioned U.S. Patent Application Serial No. [Attorney Docket No. 13DV-13490] to Rigney et al., U.S. Patent No. 6,025,078 to Rickerby et al., U.S. Patent No. 6,117,560 to Maloney and U.S. Patent No. 4,774,150 to Amano et al., such prior uses were based on additional oxides present in limited regions of a TBC (Amano et al.), or oxides added to the binary YSZ system in which zirconia is stabilized by yttria to yield a tetragonal microstructure (Rigney et al. and Rickerby et al.) or a cubic pyrochlore microstructure (Maloney) which therefore differ from the cubic (fluorite-type) microstructures of the present invention.

[0012] The coatings of this invention can be readily deposited by PVD to have a strain-resistant columnar grain structure, which reduces the thermal conductivity and promotes the strain tolerance of the coating. Alternatively, the coatings can be deposited by plasma spraying to have microstructures characterized by splat-shaped grains.

[0013] Other objects and advantages of this invention will be better appreciated from the following detailed description.

Brief Description of Drawings

[0014] Figure 1 is a perspective view of a high pressure turbine blade.

[0015] Figure 2 schematically represents a cross-sectional view of the blade of Figure 1 along line 2--2, and shows a thermal barrier coating system on the blade in accordance with a preferred embodiment of the invention.

Detailed Description

[0016] The present invention is generally applicable to components subjected to high temperatures, and particularly to components such as the high and low pressure turbine nozzles and blades, shrouds, combustor liners and augmentor hardware of gas turbine engines. An example of a high pressure turbine blade 10 is shown in Figure 1. The blade 10 generally includes an airfoil 12 against which hot combustion gases are directed during operation of the gas turbine engine, and whose surface is therefore subjected to hot combustion gases as well as attack by oxidation, corrosion and erosion. The airfoil 12 is protected from its hostile operating environment by a thermal barrier coating (TBC) system schematically depicted in Figure 2. The airfoil 12

is anchored to a turbine disk (not shown) with a dovetail 14 formed on a root section 16 of the blade 10. Cooling passages 18 are present in the airfoil 12 through which bleed air is forced to transfer heat from the blade 10. While the advantages of this invention are particularly desirable for high pressure turbine blades of the type shown in Figure 1, the teachings of this invention are generally applicable to any component on which a thermal barrier coating may be used to protect the component from a high temperature environment.

[0017] The TBC system 20 is represented in Figure 2 as including a metallic bond coat 24 that overlies the surface of a substrate 22, the latter of which is typically a superalloy and the base material of the blade 10. As is typical with TBC systems for components of gas turbine engines, the bond coat 24 is preferably an aluminum-rich composition, such as an overlay coating of an MCrAlX alloy or a diffusion coating such as a diffusion aluminide or a diffusion platinum aluminide of a type known in the art. Aluminum-rich bond coats of this type develop an aluminum oxide (alumina) scale 28, which is grown by oxidation of the bond coat 24. The alumina scale 28 chemically bonds a TBC 26, formed of a thermal-insulating material, to the bond coat 24 and substrate 22. The TBC 26 of Figure 2 is represented as having a strain-tolerant microstructure of columnar grains 30. As known in the art, such columnar microstructures can be achieved by depositing the TBC 26 using a physical vapor deposition technique, such as EBPVD. The invention is also believed to be applicable to noncolumnar TBC deposited by such methods as plasma spraying, including air plasma spraying (APS). A TBC of this type is in the form of molten splats, resulting in a microstructure characterized by irregular flattened grains and a degree of inhomogeneity and porosity.

[0018] As with prior art TBC's, the TBC 26 of this invention is intended to be deposited to a thickness that is sufficient to provide the required thermal protection for the underlying substrate 22 and blade 10, generally on the order of about 75 to about 300 micrometers. According to the invention, the thermal-insulating material of the TBC 26 may be a two-component system of zirconia stabilized by dysprosia, gadolinium oxide, erbia, neodymia, samarium oxide or ytterbia, or a two-component system of hafnia stabilized by dysprosia, gadolinium oxide, samarium oxide, yttria or ytterbia. Three-component systems can be formed of these compositions by adding a

limited amount of yttria, generally up to five weight percent, such as about 4 to about 5 weight percent. When formulated to have a cubic (fluorite-type) microstructure, each of these compositions has been shown by this invention to have a substantially lower thermal conductivity than YSZ, particular YSZ containing six to eight weight percent yttria. These compositions also have the advantage of having a relatively wide cubic region in their phase diagrams, such that impurities and inaccuracies in the coating chemistry are less likely to lead to a phase transformation. Based on an investigation discussed below, suitable, preferred and target chemistries (by atomic percent) for the TBC 26 are set forth below in Table I. These chemistries ensure a stable cubic microstructure over the expected temperature range to which the TBC 26 would be subjected if deposited on a gas turbine engine component.

[t1]

Table I

		Stabilizer Content (at%)	Stabilizer Content (at%)
Base Material	Stabilizer	Broad Range	Preferred Range
ZrO_2	Dy_2O_3	10 to 45%	10 to 30%
ZrO_2	Er_2O_3	10 to 25%	12 to 25%
ZrO_2	Gd_2O_3	10 to 25%	10 to 20%
ZrO_2	Nd_2O_3	8 to 22%	8 to 18%
ZrO_2	Sm_2O_3	10 to 25%	10 to 20%
ZrO_2	Yb_2O_3	8 to 30%	15 to 25%
HfO_2	Dy_2O_3	10 to 50%	10 to 45%
HfO_2	Gd_2O_3	5 to 30%	10 to 25%
HfO_2	Sm_2O_3	5 to 30 %	10 to 20%

HfO_2	Y_2O_3	10 to 45%	15 to 40%
HfO_2	Yb_2O_3	10 to 50%	15 to 25%

[0019] In addition to low thermal conductivities, the hafnia-based compositions of Table I have also been shown to be resistant to the infiltration of CMAS. While not wishing to be held to any particular theory, it is believed that the high melting temperature and surface energy of hafnia leads to little or no bonding tendency to the CMAS eutectic composition, and therefore inhibits the infiltration and bonding of CMAS to the TBC 26 while CMAS is molten and therefore capable of infiltrating the TBC 26. To benefit from this capability, the hafnia-based coatings of this invention can be used alone or as the outermost layer of a multilayer TBC. Even when deposited by PVD to have a columnar grain structure as shown in Figure 2, the hafnia-based coating compositions of this invention have been observed to reject or minimize the formation and infiltration of CMAS that would otherwise result in a CTE mismatch that can lead to spallation of the TBC 26.

[0020] In an investigation leading to this invention, TBC's were deposited by EBPVD on specimens formed of the superalloy Ren é N5 on which a PtAl diffusion bond coat had been deposited. The specimens were coated by evaporating a single ingot of the desired composition. The TBC's were deposited to have thicknesses on the order of about 75 to about 150 micrometers. The chemistries and thermal conductivities of the coatings are summarized in Table II below. Thermal conductivities are reported at about 890 ° ° C following both stabilization at about 1000 ° C and a thermal aging treatment in which the specimens were held at about 1200 ° C for about two hours to determine the thermal stability of their coatings.

[t3]

Table II

				Thermal Conductivity	Thermal Conductivity
	Specimen	Stabilizer Content	Stabilizer Content	Stabilized	Aged

	(Coating)	(at.%)	(wt.%)	(W/mK)	(W/mK)
	$ZrO_2+Dy_2O_3$	15	34.8	1.13	1.19
	$ZrO_2+Er_2O_3$	17	38.9	1.14	1.13
a	$ZrO_2+Gd_2O_3$	19.6	41.0	0.95	1.21
b	$ZrO_2+Gd_2O_3$	14.3	32.0	0.96	1.20
	$ZrO_2+Nd_2O_3$	13	29.0	0.95	1.14
	$ZrO_2+Sm_2O_3$	15	33.3	n/a	n/a
	$ZrO_2+Yb_2O_3$	20	44.4	1.16	1.16
	$ZrO_2+Yb_2O_3$	20	44.4	1.11	1.17
c	$ZrO_2+Yb_2O_3$	19.5	43.0	0.95	1.03
d	$ZrO_2+Yb_2O_3$	18.9	42.0	1.09	1.17
	$HfO_2+Dy_2O_3$	30	43.2	0.84	0.96
	$HfO_2+Gd_2O_3$	15	23.3	0.96	1.13
	$HfO_2+Sm_2O_3$	20	29.3	n/a	n/a
	$HfO_2+Y_2O_3$	30	31.5	n/a	n/a
	$HfO_2+Yb_2O_3$	20	31.9	1.16	1.16

[0021] a - Further alloyed to contain 4 wt.% Y_2O_3 (about 3.1 at.%).

[0022] b - Further alloyed to contain 4.8 wt.% Y_2O_3 (about 3.4 at.%).

[0023] c - Further alloyed to contain 4 wt.% Y_2O_3 (about 3.2 at.%).

[0024] d - Further alloyed to contain 4.1 wt.% Y_2O_3 (about 3.2 at.%).

[0025] The above results evidenced that the zirconia and hafnia-based TBC coatings of this invention had much lower thermal conductivities than the industry standard 6-8% YSZ material (above about 1.6 W/mK), and are significantly more thermally stable than 7%YSZ in terms of the thermal conductivities. Based on these results, it is also believed that the thermal conductivities of the zirconia and hafnia-based compositions of this invention might be further reduced by the inclusion of third and/or fourth oxides. Suitable oxides for this purpose include those evaluated above, namely, dysprosia, gadolinium oxide, erbia, neodymia, samarium oxide and ytterbia, as well as potentially zirconia (for the hafnium-based compositions), hafnia (for the zirconia-based compositions), barium oxide (BaO), calcia (CaO), ceria (CeO_2), europia (Eu_2O_3), indium oxide (In_2O_3), lanthana (La_2O_3), magnesia (MgO), niobia (Nb_2O_5), praseodymia (Pr_2O_3), scandia (Sc_2O_3), strontia (SrO), tantala (Ta_2O_3), titania (TiO_2) and thulia (Tm_2O_3).

[0026] While the invention has been described in terms of a preferred embodiment, it is apparent that other forms could be adopted by one skilled in the art. Accordingly, the scope of the invention is to be limited only by the following claims.